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54 **Poly(vinyl alcohol-vinylamine)copolymers for improved moist compressive strength of paper products.**

57 A method for preparing a paperboard product by depositing wood pulp from an aqueous slurry containing an effective amount of poly(vinyl alcohol-vinylamine) as a moist compressive strength additive mixture. Preferably the mixture consists essentially of 0.5-5 parts poly(vinyl alcohol-vinylamine) per part anionic polymer.

**EP 0 337 310 A1**

**POLY(VINYL ALCOHOL-VINYLAMINE) COPOLYMERS FOR IMPROVED MOIST COMPRESSIVE STRENGTH  
OF PAPER PRODUCTS**

TECHNICAL FIELD

The invention relates to the preparation of paper and paperboard by the deposition of wood pump from an aqueous slurry and, more particularly, relates to the improvement in the moist compressive strength of such paper products.

BACKGROUND OF THE INVENTION

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In the production of paper, paperboard and similar water-laid paper webs (hereinafter called "paper"), a cellulose fiber suspension, which may contain rosin size and mineral constituents (fillers) depending on the product desired, is deposited and drained on a continuously moving wire cloth. In this process, the free water passes through the paper web which undergoes further processing to yield the desired paper product.

Paperboard cartons which are stored or stacked under conditions of high humidity (90+%) absorb a high level of moisture of approximately 14-17%. This absorbed moisture causes the cartons, especially those near the bottom of the stack, to buckle or yield with the stack tumbling and causing damage to the contents.

One solution to this problem would be to increase the weight of the boxboard components, but packagers prefer to use lighter weight and stronger cartons.

thus, there is a need for means for improving the moist compressive strength of paper products.

U.S. 3,597,314 discloses a process for dewatering aqueous cellulose fiber suspension in the formation of paper by adding to the suspension from 0.05 to 4% of a water soluble polymer consisting essentially of units derived from N-vinyl-N-methylformamide having 60-100% of the formic acid radicals of the polymer split off by acid hydrolysis.

H. H. ESPY, TAPPI Proceedings, 1983, Papermakers Conference, pp.191-195 discloses that combinations of carboxymethyl cellulose (CMC) and poly(aminoamide) epichlorohydrin (PAE) wet strength resin improve wet and dry strength more than PAE resin alone.

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SUMMARY OF THE INVENTION

The present invention provides a means for increasing the moist compressive strength of a paper product prepared by depositing cellulose fiber from an aqueous slurry. The improvement comprises adding to the aqueous slurry of cellulose fiber an effective amount of a moist compressive strength additive consisting essentially of poly(vinyl acetate-vinylamide), preferably in combination with an anionic polymer, such as carboxymethyl cellulose in a ratio of 0.5 to 5 parts by weight cationic polymer to one part anionic polymer. The vinyl acetate units of the poly(vinyl acetate-vinylamide) are at least 75 mole%, preferably 90 mole%, hydrolyzed to vinyl alcohol units and the vinylamide units are hydrolyzed to provide the polymer with 1-50 mole% vinylamine units.

In addition to improving the moist compressive strength of the paper product, such paper products are more readily repulpable because the wet tensile strength is lower than that normally achieved through the use of the PAE wet strength resins.

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DETAILED DESCRIPTION OF THE INVENTION

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The means for improving the moist compressive strength of paper products is incorporated into the wet-end stage of the papermaking process. An amount of additive composition effective to increase the moist compressive strength of the paper product, for example 0.1 to 3 wt% based on cellulose fibers, is added to the aqueous slurry of cellulose fiber, such as wood pulp. The added composition consists

essentially of a poly(vinyl alcohol-vinylamine) [P(VOH-VAm)], preferably in combination with a carboxymethyl cellulose (CMC). The most preferred composition will contain 0.5-5 parts of P(VOH-VAm) per part of anionic polymer, preferably about 2 parts P(VOH-VAm) per part anionic polymer.

The P(VOH-VAm) is a poly(vinyl acetate-vinylamine) in which the vinyl acetate units are hydrolyzed to at least 75 mole%, preferably 90+ mole%, to vinyl alcohol units and most preferably about 99+ mole% hydrolyzed, i.e. fully hydrolyzed. The amount of the vinylamide units in the polymer which should be hydrolyzed depends on the mole ratio of poly(vinyl acetate) to poly(vinylamide), but should be sufficient to give at least 1 mole% vinylamine units based on total polymer, preferably 3 to 30 mole%, and most preferably 6 to 12 mole%. Thus, the P(VOH-VAm) component in the additive composition may contain amounts of unhydrolyzed vinylamide and/or vinyl acetate units. Suitable P(VOH-VAm) polymers will contain about 1-50 mole%, preferably 3-30 mole% vinylamine units with the remainder being vinyl alcohol units and, in the case where the polymer is less than fully hydrolyzed, amounts of vinylamide and vinyl acetate units. The molecular weight of P(VOH-VAm) can range from 6,000 to 300,000, preferably 10,000 to 100,000.

The process for preparing P(VOH-VAm) suitable for use in the present invention is the same as the well known process for making polyvinyl acetate and hydrolyzing it to polyvinyl alcohol with merely the incorporation of a vinylamide monomer into the polymerization reaction. The vinylamide monomer may be a vinylacetamide or preferably a vinylformamide, especially N-vinylformamide.

Representative references for making P(VOH-VAm) are W. M. Brouwer, et al., J. Polym. Sci., Polym. Chem. Ed., 22, 2353 (1984) and C. J. Bloys van Treslong, et al., Eur. Polym. J., 19(2), 131-4 (1983).

The preferred method for making P(VOH-VAm) is disclosed in copending application Serial No. 181,873 entitled "Method For Preparing Poly(vinyl alcohol)-Co-Poly(vinylamine) Via a Two-Phase Process" filed on even date herewith.

In addition to P(VOH-VAm), the moist strength additive composition preferably includes an anionic polymer such as anionic starch, carboxymethyl guar, polyacrylic acid, partially hydrolyzed polyacrylamide or most preferably CMC. The degree of carboxymethyl substitution in the CMC can range from 0.2 to 1.2 and the molecular weight can range from 10,000 to 300,000.

The amount of the moist strength additive composition added to the slurry of cellulose fibers is about 0.1-3 wt% based on fiber and is preferably about 0.2-2 wt%. the P(VOH-VAm) is added to the slurry before the addition of the anionic polymer. If the two components are mixed together before adding them to the slurry, a gummy mixture results. It is preferred to add the P(VOH-VAm) and the anionic polymer as aqueous solutions.

It is believed that the P(VOH-VAm) being cationic is absorbed by the anionic cellulose fibers and, especially with addition of the anionic polymer, electrostatic bonds are formed leading to polyelectrolyte complexes which enhance the strength of the fiber matrix through stronger interfiber bonds.

By forming such polyelectrolyte complexes through electrostatic bonds and reducing the susceptibility of the fiber's structure to the weakening effects of moisture, the treated paper is better able to withstand compaction forces, e.g. when cartons formed from such treated components are stacked under conditions of high humidity and high moisture content. Yet the interfiber bonds can still be broken during typical repulping processes.

#### EXAMPLE 1

For the following Runs, Southern pine unbleached kraft pulp was beaten in tap water to a Canadian Standard Freeness (CSF) of 400 mL. The beaten pulp was then classified (fines removed) resulting in a final freeness of 700 mL. (The purpose of classifying the pulp was to avoid variable interactions of the polymer and fines fraction which could affect fines retention and, hence, strength properties.). The pulp was subsequently dewatered to approximately 25% solids and stored at 40° F in the presence of a small amount of preservative until used in handsheets. Immediately prior to handsheet preparations, the dewatered pulp was suspended at 1.5% consistency in tap water using a British disintegrator. The pulp was then diluted to 0.5% consistency and an amount equivalent to 30 g (oven dry basis) was utilized in preparing each set of handsheets. Solutions of several P(VOH-VAm) were prepared at approximately 0.25% solids by first stirring and then aging the suspensions overnight in distilled water at room temperature. The resulting solutions were filtered through a 325-mesh sieve to remove undissolved polymer. Low-viscosity CMC (D.S. = 0.7) was dissolved at 1% solids in distilled water (by cooking at 85° C for 20 minutes) for use in handsheets. A commercial grade of PAE (Kymene brand from Hercules, Inc.) was diluted to 1% solids prior to pulp addition. In those cases where polymer combinations were involved, a measured amount of the

cationic component was first stirred into the pulp for 5 min followed by CMC and an additional 5 min of stirring. An aliquot of pulp sufficient to form one 2.5 g handsheet (63 g/m<sup>2</sup>) was added to a Noble & Wood mold where the forming consistency was 0.04%.

The handsheets were formed on a 100 mesh monel wire, couched onto blotter stock, pressed 5 min at 50 psig, and dried 7 min on a steam drum at 220 °F. Control handsheets were formed from untreated pulp and from pulp treated with the additives as shown in Tables 1 and 2. After conditioning at 50% RH and 73 °F, the handsheets were tested for basis weight, wet tensile, and dry and moist compressive strength. Moist compressive strength and wet tensile factors were determined by dividing the value of the treated sheet by that of the untreated controls. Table 1 shows the amount of cationic and anionic additives in the fiber slurry as well as the performance data for the paper product prepared from a commercial southern pine pulp formulation at pH 7-9. The Runs in Table 2 used a fiber slurry maintained at pH 4.5 throughout the sheetmaking process through addition of dilute sulfuric acid.

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TABLE 1

pH 7-9		ADDITIVES (% BASED ON FIBER)		P(VOH-VAm)		MOL. WT. (Mn x 10 <sup>3</sup> )	BASIS WT	COMPRESSIVE STRENGTH		MOIST COMPRESSIVE STRENGTH FACTOR	WET TENSILE FACTOR
RUN				% AMINE FUNCTIONALITY	% HYDROXYL FUNCTIONALITY			STFL DRY	Lb F/in MOIST		
1		Blank Control	-	-	-		62.9	7.13	2.86	1.0	1.0
2		PAE (1)	-	-	-		65.8	8.79	3.01	1.05	9.8
3		PAE (1.5)	-	-	-		61.4	8.36	3.02	1.05	12.7
4		PAE (1); CMC (0.4)	-	-	-		64.9	10.12	3.75	1.31	17.8
5		P(VOH-VAm)(1)	12	88	88	36	62.6	8.84	4.68	1.64	6.84
6		": CMC (0.1)	12	88	88	36	62.5	9.23	4.79	1.67	7.50
7		": CMC (0.2)	12	88	88	36	64.9	9.78	5.08	1.78	7.39
8		": CMC (0.4)	12	88	88	36	62.5	8.75	4.96	1.73	6.88
9		P(VOH-VAm)(1)	30	70	70	9	64.7	8.29	4.74	1.66	5.13
10		": CMC (0.1)	30	70	70	9	62.2	9.01	5.00	1.75	7.29
11		": CMC (0.2)	30	70	70	9	63.0	9.45	5.19	1.81	8.68
12		": CMC (0.4)	30	70	70	9	69.4	10.51	5.50	1.92	8.31
13		P(VOH-VAm) (1)	6	94	94	80	62.3	8.44	3.35	1.16	5.24
14		": CMC (0.1)	6	94	94	80	62.8	9.18	3.64	1.26	7.19
15		": CMC (0.2)	6	94	94	80	62.6	9.35	3.74	1.29	7.50
16		": CMC (0.4)	6	94	94	80	63.7	9.31	4.17	1.44	7.34

TABLE 2

pH 4.5		ADDITIVES (% BASED ON FIBER)	P(VOH-VAm)		MOL. WT. (Mn x 10 <sup>3</sup> )	BASIS WT	COMPRESSIVE STRENGTH		MOIST COMPRESSIVE STRENGTH FACTOR	WET TENSILE FACTOR
RUN			% AMINE FUNCTIONALITY	% HYDROXYL FUNCTIONALITY			STFI, DRY	Lb F/in MOIST		
17		Blank Control	--			62.6	6.43	3.81	1.0	1.0
18		PAE (1)	--			61.6	7.59	3.67	0.96	13.7
19		PAE (1); CMC (0.4)	--			69.0	10.4	5.08	1.33	22.1
20		P(VOH-VAm)(1)	3	97	36	63.7	7.99	3.88	1.02	4.4
21		" ; CMC (0.1)	3	97	36	67.2	8.57	4.54	1.19	4.5
22		" ; CMC (0.2)	3	97	36	84.9	8.11	4.17	1.09	4.1
23		" ; CMC (0.4)	3	97	36	62.5	7.60	3.75	0.98	3.8
24		P(VOH-VAm)(1)	12	88	36	66.2	8.03	4.34	1.14	5.3
25		" ; CMC (0.4)	12	88	36	62.9	8.79	4.43	1.16	5.8
26		" ; CMC (0.8)	12	88	36	66.4	8.74	4.66	1.22	5.2
27		" ; CMC (1.2)	12	88	36	82.4	8.42	4.82	1.27	4.5
28		P(VOH-VAm) (1)	30	70	9	63.1	7.93	4.52	1.19	5.1
29		" ; CMC (0.4)	30	70	9	68.7	9.81	5.25	1.38	6.9
30		"(0.5); CMC (0.5)	30	70	9	68.4	8.91	4.65	1.22	6.6
31		" ; CMC (1.0)	30	70	9	61.6	8.09	4.34	1.14	5.6
32		" ; CMC (1.5)	30	70	9	63.2	8.29	4.45	1.17	4.9

It can be seen from the data in Table 1 that the resulting paper product according to the present invention (Runs 5-16) provided dry and moist compressive strengths and wet tensile strength superior to those of the untreated control paper product. The combination of the P(VOH-VAm) and CMC provided paper product superior to those prepared using P(VOH-VAm) alone. (CMC, by itself, has little or no beneficial effect on paper strength properties when added to the fiber suspension.) The addition of 1% P(VOH-VAm) coupled with 0.2 or 0.4% CMC produced maximum or near maximum compressive strength properties.

From Table 2 it can be seen that the performance of P(VOH-VAm) in combination with CMC is somewhat lower at acid pH compared to that under alkaline pH.

The wet tensile level produced by the P(VOH-VAm) was lower than normally achieved through the use of PAE wet strength resins in combination with CMC and suggests that P(VOH-VAm)-treated papers may be more readily repulped which is a desirable property.

## EXAMPLE 2

A repulpability study was conducted using various handsheet sets made with (a) no additive (blank control), pH 4.5; (b) PAE (1%), pH 4.5; (c) PAE (1%) and CMC (0.4%), pH 4.5; (d) P(VOH-VAm) (1%), pH 4.5; (e) P(VOH-VAm) (1%), pH 7-8; and (f) P(VOH-VAm) (1%) and CMC (0.4%), pH 7-8. The P(VOH-VAm) had 6% amine functionality and a molecular weight of 130,000.

The handsheets containing the P(VOH-VAm) [(d), (e) and (f)] all repulped considerably better than the reference sheets [(b) and (c)]. The handsheets formed at pH 7-8 containing P(VOH-VAm) alone or with CMC present had more undispersed fiber than P(VOH-VAm) at pH 4.5. Results from visual inspection of the diluted fiber slurries correlate with the above observations.

Thus, the combination of high dry and moist compressive strengths coupled with better repulpability afforded by the use of P(VOH-VAm) represents a distinct advantage over combinations containing PAE.

## STATEMENT OF INDUSTRIAL APPLICATION

The use of P(VOH-VAm) preferably with CMC as additives in the wet end stage of a paper making process yields a paper product having improved moist compressive strength.

## Claims

1. In a method for preparing a paper product by depositing cellulose fiber from an aqueous slurry thereof, the improvement for increasing the moist compressive strength of the paper product which comprises adding to the aqueous slurry of cellulose fiber an effective amount of an additive consisting essentially of a cationic poly(vinyl acetate-vinylamine), the vinyl acetate units being at least 90 mole% hydrolyzed to vinyl alcohol units and containing 1-50 mole% vinylamine units.

2. The method of Claim 1 in which the copolymer contains 3 to 30 mole% vinylamine units.

3. The method of Claim 1 in which the vinyl acetate units of the copolymer are about 99 + mole% hydrolyzed to vinyl alcohol units.

4. In a method for preparing a paper product by depositing cellulose fibers from an aqueous slurry thereof, the improvement which comprises adding to the aqueous slurry of cellulose fibers an effective amount of a moist compressive strength additive composition consisting essentially of 0.5-5 parts by weight poly(vinyl acetate-vinylamide), the vinyl acetate units being at least 90 mole% hydrolyzed and the vinylamide units being hydrolyzed such that the polymer is 1-50 mole% vinylamine units, per part anionic polymer.

5. The method of Claim 4 in which the anionic polymer is anionic starch, carboxymethyl guar, carboxymethyl cellulose, polyacrylic acid or partially hydrolyzed polyacrylamide.

6. The method of Claim 4 in which the anionic polymer is carboxymethyl cellulose.

7. The method of Claim 4 in which the vinyl acetate units are about 99 + mole% hydrolyzed to vinyl alcohol units.

8. The method of Claim 4 in which the cationic polymer is 3-30 mole% vinylamine units.



9. The method of Claim 4 in which the additive composition consists essentially of about 2 parts poly-(vinyl acetate-vinylamide) per part anionic polymer.

10. In a method for preparing a paper product by depositing cellulose fibers from an aqueous slurry thereof, the improvement which comprises adding to the aqueous slurry of cellulosic fibers 0.1 to 3 wt%,  
 5 based on fiber, of a moist compressive strength additive composition consisting essentially of 0.5-5 parts by weight poly(vinyl acetate-vinyl-amide), the vinyl acetate units being at least 90 mole% hydrolyzed, and the vinylamide units being hydrolyzed so that the polymer is 1-50 mole% vinylamine units, per part carboxymethyl cellulose.

11. A paper product prepared according to any of the claims 1 to 10.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 216 387 (BASF) * Abstract; column 4, line 23 - column 5, line 31; examples 1-4 * ---	1,2,11	D 21 H 3/38 D 21 D 3/00
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 54, no. 8, February 1984, abstract no. 9112, Appleton, Wisconsin, US; & JP-A-83 17 827 (KURARAY CO., LTD) 02-02-1983 * Whole abstract * ---	1-3,11	
A	US-A-3 702 800 (A.G. TSUK et al.) * Whole document * ---	1,2,11	
A	GB-A-1 110 004 (BADISCHE ANILIN- & SODAFABRIK) * Whole document * ---	4-6,10,11	
A	US-A-3 320 066 (L.G. GARTH) * Whole document * ---	4-6,10,11	
A	CA-A-1 110 019 (MITSUBISHI CHEMICAL INDUSTRIES) * Pages 1-7 * ---	4,5,11	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US-A-2 745 744 (C.L. WEIDNER et al.) -----		C 08 F D 21 D D 21 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-06-1989	Examiner NESTBY K.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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